Halogens and the Halides

Halogens and Halides

Molecular Properties of Halogens

Stability of halides in various oxidation states

Lewis acidity of p-block halides

Structure and reactivity of p-block halides

Interhalogen compounds - their preparation, structures and stabilities

Oxo-acids and their salts

The Halogens (Salt Formers)

Element	State at Room Temperature	Color
^{9}F	Gas	Pale yellow 
^{17}Cl	Gas	Yellow-green 
^{35}Br	Liquid	Red 
^{53}I	Solid	Black / Violet 
^{85}At	Radioactive	

Halogens

- Highly reactive – do not occur in free elemental state
- Non-polar diatomic molecules
  - Reactivity: $F_2 > Cl_2 > Br_2 > I_2$
- Reaction of X_2 with compounds M-M, M-H, M-C result in formation of M-X bonds M = metal or non-metal
- Can form charge transfer complexes with certain solvents
- Volatile
- Colour of elements and compounds increase with atomic number
- Ions widespread and abundant
- Crustal abundance: $F^- > Cl^- > Br^- > I^-$

Atomic Properties of the Halogens

X	**Electronic Configuration**	**1st IE** /kJ mol^{-1}	**EA** /kJ mol^{-1}	**$\Delta H_{dissoc.}$** /kJ mol^{-1}	**Van der Waal's Radius** /pm	**Ionic radius** **X^-** /pm
F	$1s^2 2s^2 2p^5$	1680.6	332.6	158.8	135	133
Cl	$[Ne]3s^2 3p^5$	1255.7	348.7	242.6	180	184
Br	$[Ar]3d^{10} 4s^2 4p^5$	1142.7	324.5	192.8	195	196
I	$[Kr]4d^{10} 5s^2 5p^5$	1008.7	295.3	151.1	215	220
At	$[Xe]4f^{14} 4d^{10} 6s^2 6p^5$	926	270	-	-	-

Greenwood, N.N.; Earnshaw, A. ***Chemistry of the Elements,*** 2nd Ed. p. 800

Fluorine

- Name derived from fluorspar CaF – emits light when heated
- Highly toxic – 50 ppm
- Causes severe skin burns
- At least two chemists, Paulin Louyet and Jerome Nickles died as a direct result of attempts to isolate fluorine
- In 1886, H. Moissan isolated F_2 – electrolysis of KHF_2/HF
- Most electronegative element
- Most reactive element (reacts with practically all inorganic and organic substances, sometimes explosively)
- Extremely strong oxidising agent – produces high oxidation states in other reactant elements

Fluorine Uses

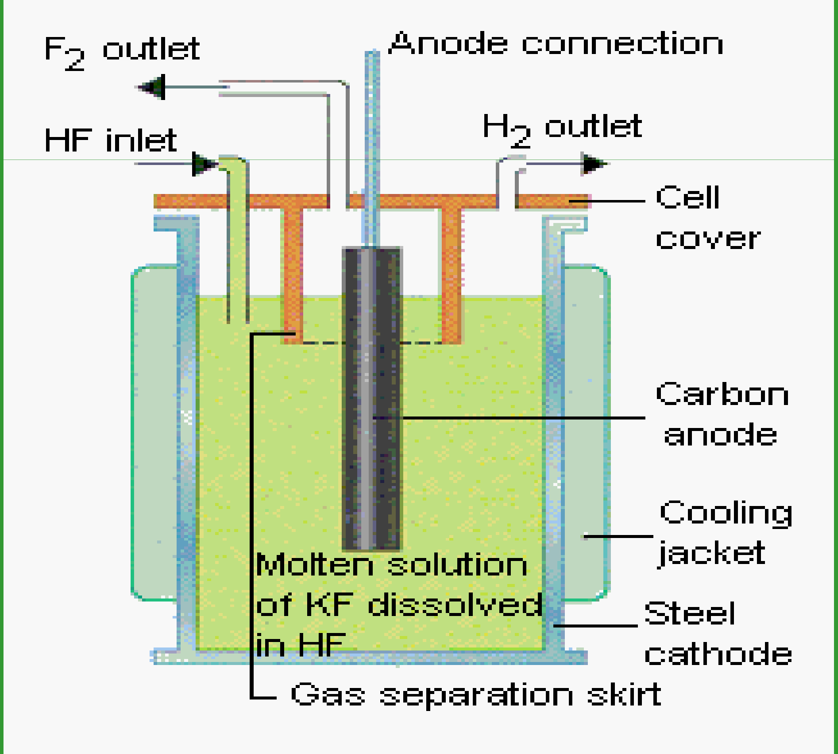
- Used in rocket fuel
- To produce UF_6 for nuclear power generation
- Production of SF_6 for dielectrics
- To manufacture fluorinating agents ClF_3, BrF_3 and IF_5

Synthesis of F_2

- Large Scale

Electrolysis of KF dissolved in anhydrous HF

$$2\ KHF_2(s) \rightarrow H_2(g) + F_2(g) + 2\ KF(s)$$



http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch10/group7.php

Synthesis of F_2

- Only Chemical synthesis – small scale – Christe 1986

$$K_2MnF_6 + 2SbF_5 \xrightarrow{150^{o}C} KSbF_6 + [MnF_4]$$

$$\downarrow$$

$$MnF_3 + \frac{1}{2} F_2$$

The stronger Lewis acid SbF_5 can displace the weaker one MnF_4 from its salt. MnF_4 which is unstable, decomposes rapidly to a lower oxidation state, thus liberating F_2

Chlorine

- First halogen to be isolated – Scheele 1774

$$4NaCl + 2H_2SO_4 + MnO_2 \rightarrow Cl_2 + 2Na_2SO_4 + MnCl_2 + 2H_2O$$

- Name chlorine derived from the colour of the gas (chlorus) yellowish or light green

- Toxic – rapid death at 1000 ppm
- NaCl – most abundant compound, main chlorine source, known from earliest times, used as payment

- Used as a bleaching agent, disinfectant, germicide

- ~ 15000 chlorinated compounds currently used

Chlorine Synthesis

Industrial

- Electrolysis of brine

$$Na^+ + Cl^- + H_2O \rightarrow \tfrac{1}{2}\,Cl_2 + \tfrac{1}{2}\,H_2 + Na^+ + OH^-$$

- Electrolysis of molten NaCl

$$2\,NaCl \rightarrow Cl_2 + 2\,Na$$

Small scale Lab Synthesis

$$4HCl + MnO_2 \rightarrow Cl_2 + MnCl_2 + 2H_2O$$

$$16HCl + 2KMnO_4 \rightarrow 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O$$

Bromine

- Isolated in 1826 by A.J. Balard (aged 23)
- Named for its unpleasant smell (Greek for stink)
- Only non-metallic element existing as a liquid at room temp.
- Major use – to make ethylene dibromide – gasoline additive that acts as a lead scavenger
- Synthesis of MeBr – nematocide, pesticide
- Compounds used in photography (AgBr, medicine (KBr – sedative, anti-convulsant), flame retardant, phase transfer catalyst, water sanitation, pharmaceuticals

Bromine Synthesis

Industrial

- Oxidation of bromides with Cl_2

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

Small scale

- Oxidation of bromides with MnO_2 in acid solution

$$2Br^- + 4H^+ + MnO_2 \rightarrow Br_2 + 2H_2O + Mn^{2+}$$

Iodine

- Isolated from seaweed in 1811 by B. Courtois

- Solid sublimes to violet vapour at atmospheric pressure

- Named for its colour (greek violet coloured)

- Slight solubility in water
- Can form complexes with various electron donating solvents

- Used in photograpy, medicine, analytical techniques, synthesis, catalysts for synthetic rubber manufacture, animal and fowl feed supplements, colourants

Iodine Synthesis

Industrial

- Oxidation of iodides

  with Cl_2

  $$2KI + Cl_2 \rightarrow 2\ KCl + I_2$$

  with MnO_2 in acid solution

  $$2I^- + 4H^+ + MnO_2 \rightarrow I_2 + 2H_2O + Mn^{2+}$$

- Reduction of Iodate to I^- followed by oxidation

  $$IO_3^- + 3HSO_3^- \rightarrow I^- + 3SO_4^{2-} + 3H^+$$

  $$5I- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Astatine

- Radioactive

- First isotope ^{211}At (t ½ 7.2 h) made in 1940 by Corston, Mackenzie and Segré

$$^{209}_{83}\mathrm{Bi} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{211}_{85}\mathrm{At} + 2\,{}^{1}_{0}\mathrm{n}$$

- Isotopes of natural radioactive series - t ½ < 1 min

- Synthetic isotopes have half lives up to 8.1 hrs

Charge Transfer Complexes

- May form with solvents that are electron pair donors eg. ROH, R_2O and RNH_2, pyridine, etc
- Eg. Solutions of iodine (electron acceptor) in various electron donating solvents can have a variety of colours depending on the electron donating ability of the solvent

Interhalogen Compounds

Compounds resulting from combinations of halogens with each other

- Four stoichiometries – XY, XY_3, XY_5, XY_7
  - where X = heavier halogen
- Diamagnetic
- Have even number of atoms
- Most are volatile

Diatomic Interhalogens XY

- 6 known compounds – ClF, BrF, IF, BrCl, ICl, IBr
- Variable stability
- Can be synthesized by direct controlled reaction of the appropriate elements (not necessarily pure)

$$X_2 + Y_2 \rightarrow XY$$

- Properties intermediate between those of parent halogens
- Chemical reactions classified as
  - Halogenation reactions
  - Donor acceptor interactions
  - Use as solvent systems

Reactions of ClF

- Strong fluorinating agent
  - Reacts with metals and non-metals at RT and above to form fluorides and Cl_2

$$W + 6ClF \rightarrow WF_6 + 3\,Cl_2$$

$$Se + 4ClF \rightarrow SeF_4 + 2\,Cl_2$$

- Acts as a chlorofluorinating agent
  - addition across a multiple bond

$$CO + ClF \rightarrow COFCl$$

$$RCN + 2ClF \rightarrow RCF_2NCl_2$$

- Reactions with OH or NH groups result in exothermic elimination of HF and chlorination of the substrate

$$HOH + 2ClF \rightarrow 2HF + Cl_2O$$

$$HONO_2 + ClF \rightarrow HF + ClONO_2$$

$$HNF_2 + ClF \rightarrow HF + NF_2Cl$$

Reactions of ClF Cont'd

- Lewis acid behaviour (fluoride ion acceptor)

$$\mathrm{NOF + ClF \rightarrow [NO]^+[ClF_2]^-}$$

$$\mathrm{MF + ClF \rightarrow M^+[ClF_2]^-}$$

where M = alkali metal or NH_4

Lewis base behaviour (fluoride ion donor)

$$\mathrm{BF_3 + 2ClF \rightarrow [Cl_2F]^+[BF_4]^-}$$

$$\mathrm{AsF_5 + 2ClF \rightarrow [Cl_2F]^+[AsF_6]^-}$$

Tetra-atomic Interhalogens XY

ClF_3, BrF_3, IF_3, ICl_3

Synthesis

ClF_3 – in gas phase at 200-300^{o}C, Cu or Ni apparatus:

$$Cl_2 + F_2 \rightarrow 2ClF_3$$

OR

$$ClF + F_2 \rightarrow ClF_3$$

BrF_3 – at room temp

$$Br_2 + F_2 \rightarrow 2BrF_3$$

OR

$$BrF + F_2 \rightarrow BrF_3$$

Tetra-atomic Interhalogens XY

- IF_3 only stable below -30°

$$I_2 + 3XeF_2 \rightarrow 2IF_3 + 3Xe$$

ICl_3 dimerises to I_2Cl_6

- $$I_2 + 3Cl_{2(l)} \xrightarrow[-80^o]{X.S\ Cl_{2(l)}} I_2Cl_6$$

- Note: I_2Cl_6 readily dissociates into ICl and Cl_2

ClF_3

- One of the most reactive compounds known
- Explosive reaction with water and organic substances
- Reacts violently with many ‘inert’ substances
- Ignites asbestos
- Used in bomb attacks in WW2
- Converts most chlorides to fluorides
- Acts both as Lewis acid and base
- Sequence of reactivity of halogen fluorides:
- $ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF > IF_3 > IF$

Halides

Ionic

- most metal halides ie. Gps 1, 2, $Ln^{2+,3+}$, $Ac^{2+,3+}$
  - Some covalent character
  - Greater difference in electronegativity, greater ionic character
  - F^- ion smallest and least polarizable of all anions
  - Cl^-, Br^-, I^- larger, more polarizable

Molecular

- Non- metals, most electronegative elements, metals in high oxidation states (≥ 3)

Organic

Preparation of Anhydrous Halides

- Halogenation of the Elements

$$E + X_2 \rightarrow EX_n$$

n dependent on halogen and reaction conditions

- Halogen Exchange
- Important for synthesis of fluorides and organic fluorine compounds

$$RCl + MF \rightarrow RF + MCl$$

$$C_6H_5CCl_3 + SbF_3 \rightarrow C_6H_5CF_3 + SbCl_3$$

Preparation of Anhydrous Halides

- Halogenation by Halogen Compounds
  - Important for metal fluorides and chlorides
  - Involve mainly treatment of oxides with halogen compounds

$$NiO + ClF_3 \rightarrow NiF_2$$

$$Sc_2O_3 + CCl_4 \xrightarrow{600^o\ C} ScCl_3$$

- Dehydration of Hydrated halides

$$[Cr(H_2O)_6]Cl_3 + 6\ SOCl_2 \xrightarrow{\text{Reflux}} CrCl_3 + 12\ HCl + 6SO_2$$

Hydrogen Halides

Hydrogen Fluoride

$$CaF_{2\,(s)} + H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + 2HF(g) \qquad 200 – 250^oC$$

- Colourless, volatile liquid
- Main source of F_2
- Highly toxic – maximum exposure 2-3ppm
- Extremely Corrosive
- Anhydrous HF attacks glass and quartz; safely handled using fluorinated plastics
- HF used to make numerous inorganic compounds, in biochemical research, glass etching, production of teflon, chlorofluorocarbons
- Weak acid in aqueous solution

Hydrogen Halides

- <u>Hydrogen Chloride</u>

$$H_2 + Cl_2 \rightarrow 2HCl \quad \text{heat}$$

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \quad {\sim}150^{o}C$$

- Colourless to slightly yellow pungent gas
- Fumes on contact with atmosphere
- Uses - Hydrochlorination of rubber
  - Production of Al_2O_3, TiO_2
  - Metallurgical processes for isolating and refining metals : Ge, Sn, V, Mn, Ta, W, Ra
  - Pickling of steel
  - Desulfuring of petroleum
  - Etching of semiconductor crystals,
  - Manufacture of vinyl chloride
  - Pigments for paint

Hydrogen Halides

- Hydrogen Bromide

$$H_2 + Br_2 \rightarrow 2HBr \quad 200\text{-}400^{o}C, Pt$$

$$NaBr(s) + H_2SO_4 \rightarrow HBr(g) + NaHSO_4(s)$$

Colourless, pungent gas

Fumes on contact with atmosphere

Used as a catalyst for organic reactions, synthetic chemistry

Hydrogen Halides

- Hydrogen Iodide

$$H_2 + I_2 \rightarrow 2HI \quad \text{heat}$$

$$2I_2 + N_2H_4 \rightarrow 4HI + N_2$$

- Colourless, pungent gas
- Fumes on contact with atmosphere
- Used to make hydriodic acid, organic and inorganic iodides, as a reducing agent, in disinfectants

Hydrogen Halides

- Anhydrous HX used for halogenation
  - Most metals, exothermic reaction
- Aqueous HX – strong acids (except HF)
  - Acid strength increases down the group

- Extent of H-bonding decreases down the group

Halides of Group 13

Boron

- BX_3 most stable
- Volatile, highly reactive
- Are monomeric trigonal planar molecules
- Melting points and volatilities mirror the parent halogens
- Used as Lewis acid catalysts
- Used in chemical vapour deposition (CVD)

BF_3

- Colourless gas

Synthesis

$$6CaF + Na_2B_4O_7 + 8H_2SO_4 \rightarrow 2\ NaHSO_4 + 6\ CaSO_4 + 7H_2O + 4BF_3$$

$$Na_2B_4O_7 + 12HF \xrightarrow{-6H_2O} [Na_2O(BF_3)_4] \xrightarrow{+2H_2SO_4} 2NaHSO_4 + H_2O + 4BF_3$$

- Forms tetrafluoroborate anion in dilute solution
  - $BF_3 + 6H_2O \rightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3$

- Powerful Lewis acid (available p orbital)
- Effective reagent in organic synthesis
- Used as catalyst in various industrial processes

BX_3

- $X = Cl, Br, I$
- Stronger lewis acids than BF_3

$$B_2O_3 + 3C + 3X_2 \xrightarrow{500^o} 6CO + 2BX_3 \quad \text{for } BCl_3 \text{ and } BBr_3$$

$$NaBH_4 + 2I_2 \rightarrow BI_3 + NaI + 2H_2$$

- Order of Lewis acid strength:

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

- Rapidly hydrolysed in water

$$BX_3 + 3H_2O \quad H_3BO_3 + 3HX$$

Stability of BX_3 adducts

Dependent on

- Chemical nature of the donor atom

- Presence of polar substituents on the ligand

- Steric effects

- Stoichiometric ratio of ligand to acceptor

Form stronger complexes with N, O and F ligands thhan with P, S and Cl

Donor atoms can also be transition metals

Eg. $[(Ph_3P)_2(CO)ClIr^I(BF_3)_2]$, $[(Ph_3P)_2Pt^0(BCl_3)_2]$

Halides of Group 13

AlX_3

- Form a large number of addition compounds /complexes
- Important in understanding Friedel-Crafts catalysis
- Adducts have varying stability

AlF_3 Synthesis

- $Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O$

- Each Al surrounded by octahedron of 6 F atoms

1:3 stoichiometry achieved by corner sharing of each F between 2 octahedra

Halides of Group 13

- $AlCl_3$
- Forms dimer at 192.4^o (mpt)

- Coordination number of Al changes from 6 (crystalline) to 4 at mpt – increased volume, reduced electrical conductivity

- $AlBr_3$ and AlI_3
- Form dimers in crystalline, liquid and gaseous phases

Halides of Group 14

Silicon – SiX_4

- Colourless, volatile reactive compounds
- Synthesis: $Si + 2X_2 \rightarrow SiX_4$
- SiF_4 – strongly fuming gas, unstable
- $SiCl_4$ – fuming liquid, stable, bpt. 146-148°
  - used to make transistor grade Si and various silicon esters
- $SiBr_4$ – fuming liquid, stable, bpt.154°
- SiI_4 – white crystals, stable, mpt. 121°, bpt. 288°

Halides of Group 14

- Tin Halides: SnX_2, SnX_4

SnX_2 – complex structural chemistry

- due to:
  - stereochemical activity of non bonding pair of electrons
  - Sn(II) can increase its coordination number by polymerization into larger structural units such as rings and chains
- Sn(II) non-bonding pair can act as donors to vacant orbitals
- Empty 5p orbital and 5d orbitals can act as acceptors in formation of covalent bonds eg. Adduct $[SnX_2(NMe)_3]$
- SnX_4 – simpler structures

Halides of Group 14

- Tin Halides: Uses
- $SnCl_2$
  - widely used reducing agent in acid solution
  - Dihydrate used in plating of plastics and silvering of mirrors
  - Perfume stabilizers in bath soaps

Halides of Phosphorus

- Forms three halide series: P_2X_4, PX_3, PX_5
- Also forms mixed halides PX_2Y, PX_2Y_3

Trihalides

- Volatile reactive compounds
- Pyramidal molecules

$$2P + 3X_2 \rightarrow 2PX_3$$

$$3CaF_2 + 2PCl_3 \rightarrow 2PF_3 + 3CaCl_2$$

PF_3

- Colourless, odourless gas
- No fumes in air
- Toxic - Forms a complex with haemoglobin
- Hydrolyses slowly with water
- Similar to CO as a ligand

PCl_3

- Most important phosphorus halide
- Main source of organophosphorus compounds
  - oil additives
  - Plasticizers
  - Flame retardants
  - Fuel additives
  - Manufacture of insecticides
- Readily oxidized to PCl_5, $POCl_3$
- Fumes in air
- Readily hydrolysed by water

Phosphorus pentahalides

- Adopt a variety of structures
- PF_5 molecular
- PCl_5 molecular in gas phase, ionic in crystalline phase, molecularly or ionically dissociated in solution

Halogen Oxides and Oxo Compounds

Chlorine Oxides

- Include Cl_2O, Cl_2O_3, ClO_2, Cl_2O_4, Cl_2O_6, Cl_2O_7
- Some used extensively in industry (Cl_2O, ClO_2)
- Important in studies of the upper atmosphere
- Strongly endothermic
- Somewhat unstable
- Cant be prepared by direct combination of the elements

Dichlorine monoxide Cl_2O

- Brownish-yellow gas at room temp. (red-brown liquid or solid at lower temps)

- Explodes when heated

- Used to make hypochlorites – $Ca(OCl)_2$

- Is an effective bleach for textiles and wood pulp

- Used to chlorinate organic compounds

- Plays a role in ozone depletion

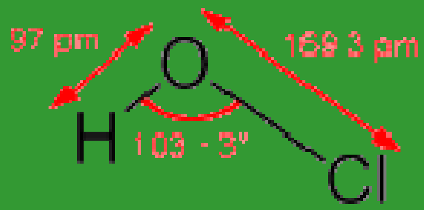
Oxoacids

- Oxoacid:
- Compound containing oxygen, at least one other element and at least one H bound to oxygen

- Produces a conjugate base by loss of H^+

Hypohalous acids HOX

HOF, HOCl, HOBr, HOI



Halogens in +1 oxidation state

HOCl - most commonly known

- Weak acid
- Considered a stronger oxidant than chlorine
- Reacts by transferring an O atom

- NaOCl most popular salt – liquid bleach
- CaOCl – solid bleach

Hypohalous acids

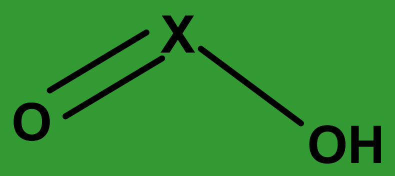
Uses

- Halogenating agents for aromatic and aliphatic compounds
- Cleavage of methyl ketones to form carboxylates and haloform

$$RCOCH_3 + 3OX^- \rightarrow RCO_2^- + 2OH^- + CHX_3$$

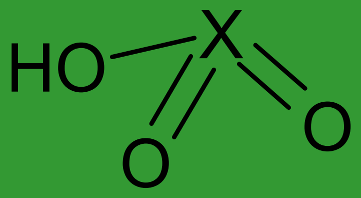
- Manufacture of hydrazine
- Bleaching and sterilizing

Halous Acids HOXO



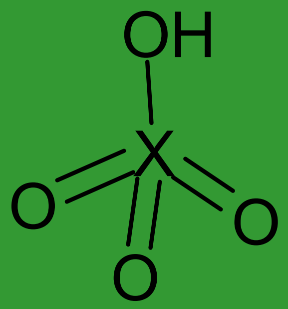
- +3 oxidation state
- Less stable than hypohalous acids
- HOBrO and HOIO have only fleeting presence in aqueous soln.
- HOClO least stable oxoacid of chlorine
- $NaClO_2$ most stable salt
  - Used for bleaching textiles
  - Source of ClO_2
  - Oxidant for removal of nitrogen oxide pollutants, malodorous and toxic compounds eg. Mercaptans, thioethers, H_2S, HCN

Halic Acids $HOXO_2$



- +5 oxidation state
- Strong acids
- Strong oxidizing agents
- Complex chemical behaviour – dependent on temp., concentration, pH

Perhalic Acids – $HOXO_3$



+7 oxidation state

Perchloric acid

- Highly corrosive, oily liquid
- Violent oxidant when heated
- Explodes on contact with easily oxidizable material
- Extremely hazardous
- Along with perchlorates are the most stable oxo compound of chlorine
- Salts often used in explosives

Perchloric Acid

- Synthesis:

$$NaClO_4 + HCl_{(l)} \rightarrow HClO_4 + NaCl$$

- In aqueous solution has very little oxidizing power
- Perchlorates known for most metals
  - Are weak ligands, monodentate, bidentate or bridging

$NaClO_4$ synthesis:

  - Electrolytic oxidation of aqueous $NaClO_3$

$$NaClO_3 \xrightarrow[PbO_2]{[O]} NaClO_4$$

Perchlorates

- Perchlorate anion often used as an inert anion in studies of metal ion complexes in aqueous solution

- Ammonium perchlorate
  - non-freezing blasting compound in mining operations
  - Oxidant in solid fuel missiles

- Magnesium perchlorate
  - Efficient desiccant – Mg^{2+} ions behave as if isolated in an inert matrix and accordingly, forms a very stable hexahydrate when in contact with water
- Potassium perchlorate
  - Used in fireworks and flares

Perbromic acid

- Was thought not to exist until 1968
- First synthesized by radiochemical synthesis: β-decay of ^{83}Se
- Chemical synthesis: oxidation of alkaline solutions of BrO_3^-, followed by passage of resulting solution through cation exchange column

$$BrO_3^- + F_2 + 2OH^- \rightarrow BrO_4^- + 2F^- + H_2O$$

- Stronger oxidizing agent than perchlorate

Periodic acids and Periodates

4 series known:

- Periodic – HIO_4
- Orthoperiodic – H_5IO_6
- Mesoperiodic – H_3IO_5
- Triperiodic – $H_7I_3O_{14}$

Interconnected in aqueous solution by a complex series of equilibria

- Involve deprotonation, dehydration and aggregation
- Concentration dependent

Periodic acids and Periodates

Periodates made by:

- oxidation (electrochemically or with chlorine) of I^-, I_2 or IO_3^- in aqueous solution.

$$IO_3^- + 6OH^- - 2e^- \rightarrow IO_6^{5-} + 3H_2O \qquad (PbO_2\text{ anode})$$

$$IO_3^- + 6OH^- + Cl_2 \rightarrow IO_6^{5-} + 2Cl^- + 3H_2O$$

- Thermal disproportionation of iodates

$$5Ba(IO_3)_2 \xrightarrow[\Delta]{} Ba_5(IO_6)_2 + 4I_2 + 9O_2$$

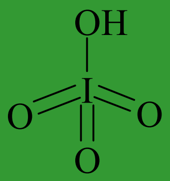
- Potent oxidants, useful in organic chemistry – cleavage of glycols, α – diketones, etc.
- Oxidation potential greatest in acidic solution; diminished with increase in ph

Periodic acid -Synthesis

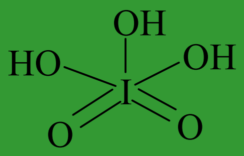
- Treatment of barium salt with conc. Nitric acid

$$\begin{tikzcd}
Ba_5(IO_6)_2 \arrow[r, "HNO_3", "-\ BaNO_3"'] & 2H_5IO_6 \arrow[r, "\text{Low pressure}\ 100^o"] \arrow[d, "\text{Dehydration at}\ 120^o"] & HIO_4\ \text{(periodic)} \\
& H_7I_3O_{14}\ \text{(triperiodic)} &
\end{tikzcd}$$

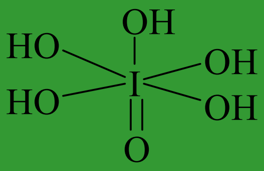
Periodic acid Structures



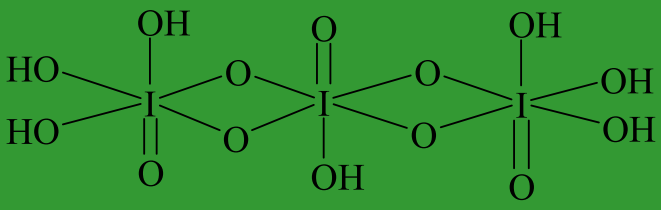
Periodic Acid



Mesoperiodic Acid



Orthoperiodic Acid



Triperiodic Acid

Oxidation states of the Halogens

- X_2 – molecular 0
- HX – hydrohalic acids and salts -1
- HOX – hypohalous acids and salts +1
- HOXO – halous acids and salts +3
- $HOXO_2$ – halic acids and salts +5
- $HOXO_3$ – perhalic acids and salts +7
- Stability of highest oxidation state increases down the group

Halogen Derivatives of Oxoacids

- Obtained by replacement of the H atom of an oxyacid with a halogen atom

- Eg. Halogen(I) perchlorates $XOClO_3$ (X = F, Cl, Br)
- Halogen(I) fluorosulfates $XOSO_2F$ (X = F, Cl, Br, I)
- Halogen(I) nitrates $XONO_2$ (X = F, Cl, Br, I)

- Halogen(III) compounds are also known

- Thermal stability decreases with increase in atomic number of the halogen

Halogen Oxide Fluorides

- Compounds in which X (Cl, Br, I) is bonded to both O and F
- X in high oxidation states due to the presence of F and O
- Variable stability

Polyhalide Anions

Binary anions

General formula XY_{2n}^{-} (n = 1,2,3,4)

Result from:

- addition of a halide ion to an interhalogen compound
- Reactions which result in halide ion transfer between molecular species

Polyhalide Anions

Ternary anions

- Gen. formula $X_mY_nZ_p^-$ (m+ n+ p odd)
- Central atom has highest atomic number
- Triatomic ions – linear
- Pentaatomic ions – square planar
- Heptaatomic ions – octahedral (distorted)
- Nonaatomic ions – square antiprismatic

- Stability enhanced by large counter-cations eg. Rb^+, Cs^+, PCl_4^+

- For a given cation, thermal stability increases with the symmetry of the polyhalide anion
- Weak oxidants

Polyiodide anions

- Numerous polyiodides crystallize from solutions containing iodide ions and iodine.

- Stoichiometry depends on the relative concentrations of the components and the nature of the cation

- I_3^- most commonly seen
- I_n^- up to I_{16}^- are known
- I_n^{2-}, I_n^{3-}, I_n^{4-} ions also known

Polyhalonium Cations

- May be tri, penta or hepta-atomic
- Fluorocations – colourless or pale yellow
  - Strong oxidizers
  - React explosively
- Other cations – orange, red or deep purple

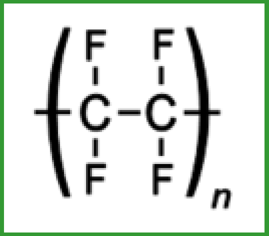
- Syntheses involve interaction of an interhalogen compound with an X^- acceptor that can be oxidized

$$2ClF + AsF_5 \rightarrow [FCl_2^+][AsF_6^-]$$

$$I_2Cl_6 + 2SbCl_5 \rightarrow 2[ICl_2^+][SbCl_6^-]$$

Polytetrafluoroethylene (PTFE) - Teflon

Synthetic fluoropolymer



- Numerous applications:
- Non-stick coating for cookware

- Containers and pipes for corrosive and reactive materials

- Automotive industry – nuts, bolts, wiper blades, clutch plates, etc…

- Coating for armour piercing bullets

- Computer mice

PTFE - Properties

- Linear molecular structure of repeating $–CF_2–CF_2–$ units
- White crystalline solid, mpt. 327°C
- Stable at low temperatures (down to -240°C)
- Low friction – coefficient of friction lower than that of any other solid
- Non-wetting – hydrophobic
- Oil resistant - oleophobic

PTFE – Properties Cont’d

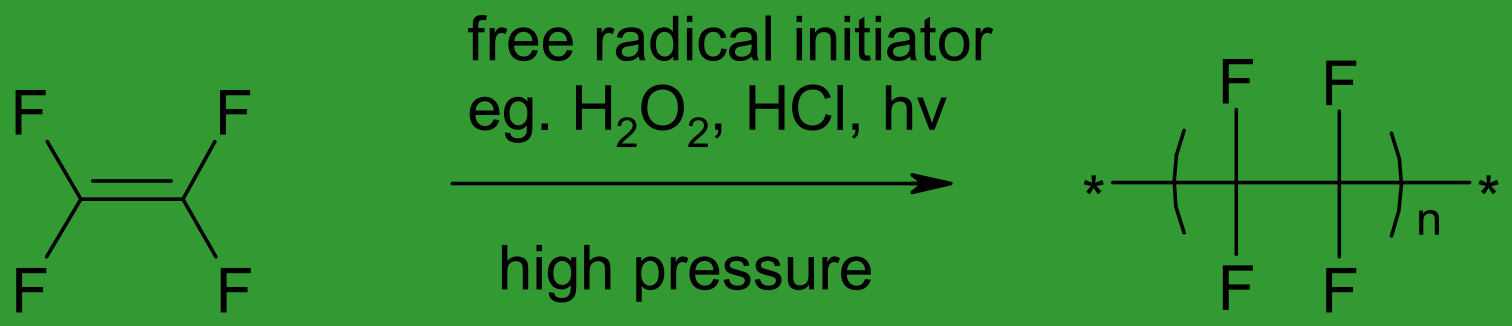
- High impact strength
- Insoluble in all solvents below 300°
- Very low adhesiveness
- Inert
- Non-flammable
- Weather resistant
- Resistant to chemical breakdown (except F_2, CF_3, molten alkali metals).

PTFE Synthesis

Emulsion polymerization

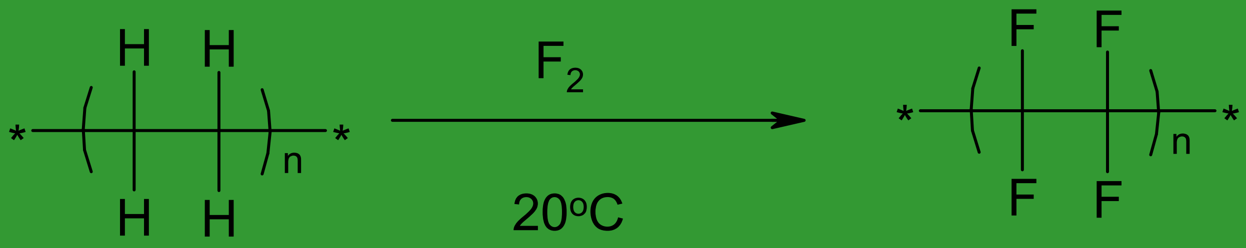
- Liquid tetrafluoroethylene is submerged in an insoluble liquid to form an emulsion.

  Carried out under pressure in the presence of free radical catalysts



PTFE Synthesis

- Reaction of polyethylene with fluorine



PTFE - Safety Concerns

- Breaks down to give off toxic chemicals at elevated temperatures

- Teflon frying pan can reach 383 ^{o}C in 5 mins

- 240^{o}C – ultra-fine particulates – toxic; kill rats

- 360^{o}C
- tetrafluoroethylene – possble carcinogen
- hexafluoropropene – eye, nose and throat irritation, decreased memory/learning
- monofluoroacetic acid – extremely toxic

PTFE - Safety Concerns

- 470^{o}C – **Silicon tetrafluoride** – toxic, corrosive gas
- 475^{o}C – **perfluoroisobutene** – toxic; fluid build up in lungs
- 500^{o}C – **Carbonyl fluoride** – irritant, chest pains, fluid in lungs
- Higher temperatures – hydrogen fluoride, trifluoroacetic acid fluoride, perfluorooctanoic acid

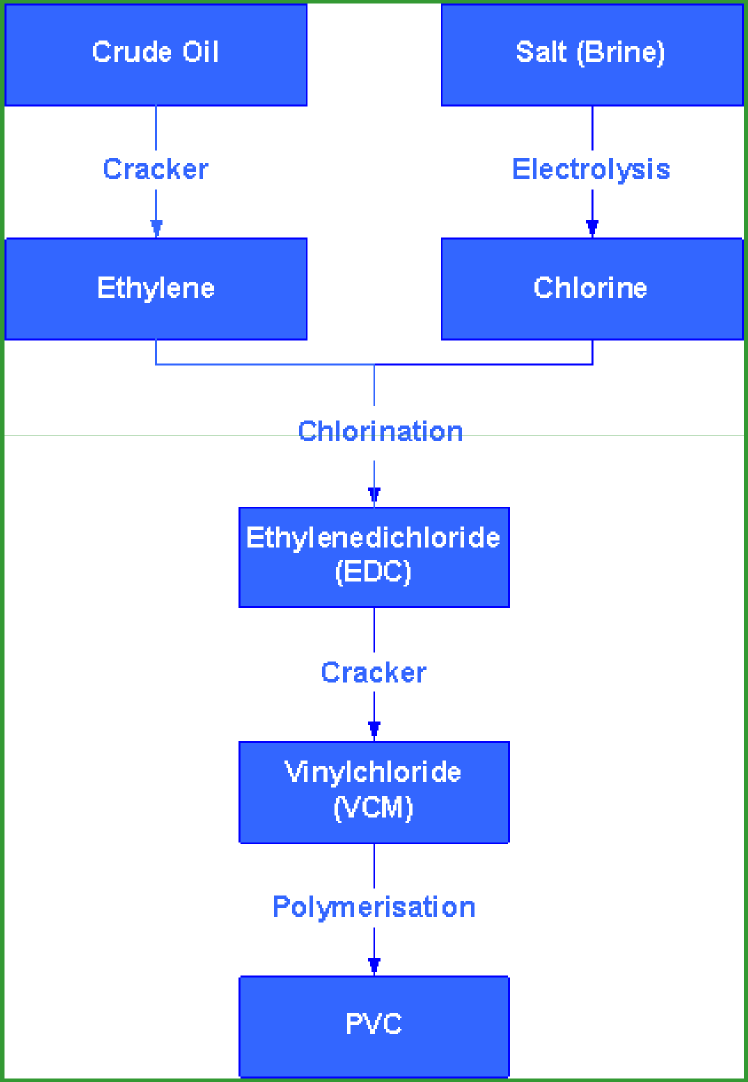
Polyvinyl chloride PVC

- Among the oldest polymers
- Widely used
- Versatile
- Tough
- Physical appearance can be varied to suit end use- eg addition of plasticizers for softness
- Flame resistant
- Durable
- Resistant to acids and alkalis, oils and greases
- Stable

PVC - Applications

- Packaging
- Toys
- Construction materials – replacing wood, concrete and clay
- Electric wires
- Medical devices

PVC - Production


Crude Oil

Cracker

Ethylene

Salt (Brine)

Electrolysis

Chlorine

Chlorination

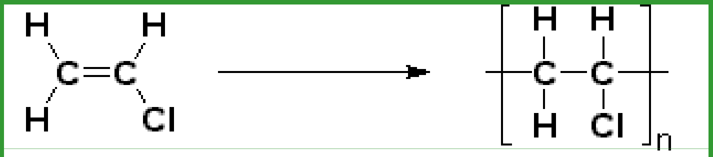
Ethylenedichloride (EDC)

Cracker

Vinylchloride (VCM)

Polymerisation

PVC



vinyl chloride

poly(vinyl chloride)

PVC - Safety

- Concern over use of plasticizers
  - Toys, blood bags, tubing

  Phthalates – preferred plasticizers – subject to leaching
  - Toxic
  - Carcinogenic

- Vinyl chloride – highly toxic, carcinogenic